

V.A.1 ElectroCat (Electrocatalysis Consortium)

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Project Start Date: February 1, 2016

Project End Date: September 30, 2020

further development of high-throughput screening techniques.

- Demonstrate 20 mA cm⁻² at 0.90 V (*iR*¹-corrected) in an H₂-O₂ fuel cell and 100 mA cm⁻² at 0.80 V in an H₂-air fuel cell (measured); maintain partial pressure of O₂ + N₂ at 1.0 bar (cell temperature 80°C).

Argonne National Laboratory

- Achieve half-wave potential agreement of < 20 mV between rotating disk electrode (RDE) and multi-electrode channel flow double electrode ORR measurements for a benchmark PGM-free catalyst.
- Select and prepare six PGM-free electrode specimens and obtain three-dimensional (3D) micro-structures using synchrotron X-ray computed tomography.
- Demonstrate current densities in the combinatorial MEA for all 25 electrodes within 10% of those in a standard 5 cm² test cell using identical PGM-free electrode compositions in both cells.
- Construct microstructure models of six PGM-free electrodes from LANL by combining X-ray computed tomography data with information from porosimetry, electron microscopy, and other characterization techniques.

Consortium Objectives

- Expedite the development of platinum group metal (PGM)-free catalysts, electrodes, and membrane electrode assemblies (MEAs) for fuel cell applications by facilitating collaboration between national laboratories.
- Foster the development of necessary capabilities.
- Create an interface for making those capabilities available to industry and academic partners.

Fiscal Year (FY) 2017 Objectives

Los Alamos National Laboratory

- Develop draft technology transfer and agreements (TT/A) plan for ElectroCat and receive feedback from member national laboratories.
- Synthesize and, in collaboration with other ElectroCat partner laboratories, characterize and evaluate oxygen reduction reaction (ORR) activity of PGM-free catalysts based on di-iron complexes.
- Synthesize and demonstrate atomic dispersion of Fe sites in (Zn, Fe)-PSIE-metal organic framework-derived catalyst; provide samples to ANL for

National Renewable Energy Laboratory

- Demonstrate F-doping onto LANL's PGM-free catalyst (e.g., Fe-CM-PANI-C catalyst) with either CF₄ or F₂.
- Demonstrate the synthesis of the M-C-N model catalyst with the chemical composition comparable to the state-of-the-art literature, and study its structural properties. The first target moiety is a nitrogen coordinated transition metal center in a carbon matrix, e.g., FeN₄ in graphene matrix.
- Demonstrate improved feasibility of segmented cell system for combinatorial PGM-free samples (e.g., Fe-CM-PANI-C catalyst) to minimize crosstalk of a one electrode layer with gradient composition and allow for a sufficient resolution and data interpretation; based on availability, demonstration performed either with standard (i.e., non-combinatorial) PGM-free samples or first generation combinatorial PGM-free samples.
- Extract values for the reaction order with respect to oxygen partial pressure and activation energy as a function of PGM-free catalyst type and/or electrode design. Utilize these extracted values to help determine the reaction mechanism for said PGM-free electrocatalyst (e.g., Fe-CM-PANI-C catalyst).

¹ *iR* is internal resistance

Oak Ridge National Laboratory

- Characterize at least three new candidate PGM-free catalysts using scanning transmission electron microscopy (STEM) imaging and analysis and X-ray photoelectron spectroscopy (XPS).
- Coordinate characterization effort at ORNL with high-throughput combinatorial results from ANL towards down-selecting potential catalysts for in-depth structural and chemical analyses.
- Coordinate 3D electron tomography effort at ORNL with 3D X-ray tomography efforts from both ANL and LANL.
- Initiate in situ microscopy studies after coordinating experimental variables with national laboratory and potential external partners.

ElectroCat Annual Milestone

- Demonstrate 20 mA cm⁻² at 0.90 V (*iR*-corrected) in an H₂-O₂ fuel cell and 100 mA cm⁻² at 0.80 V in an H₂-air fuel cell (measured); maintain partial pressure of O₂ + N₂ at 1.0 bar (cell temperature 80°C).

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan [1].

- (A) Durability (catalyst, MEA)
- (B) Cost (catalyst)
- (C) Performance (catalyst, MEA)

Technical Targets

This project focuses on the development and implementation of high-performing and durable PGM-free cathode catalysts for polymer electrolyte fuel cells, following DOE technical targets outlined in Table 3.4.7 in Section 3.4.4 (Technical Challenges) of the Multi-Year Research, Development, and Demonstration Plan [1]. The overall goal is durable PGM-free oxygen reduction reaction catalysts that achieve an activity of 0.044 A/cm² at 0.90 V in a polymer electrolyte fuel cells MEA by 2020 (Table 1).

FY 2017 Accomplishments

Consortium Development

- Established a steering committee and selected unique national laboratory capabilities relevant to PGM-free catalyst development and implementation.
- Inaugurated a public ElectroCat website in February 2016 and posted the network of national laboratory capabilities (www.ElectroCat.org).
- Established a data management plan based on Comprehensive Knowledge Archive Network and leveraging the Materials Data Facility data publication capabilities.
- Completed and approved a streamlined cooperative research and development agreement (CRADA) template and non-disclosure agreement (NDA), available for use.

Performance Improvement

- Demonstrated 83 mA/cm² at 0.80 V (120 mA/cm² at 0.8 V *V*_{*iR*-free}) in H₂-air fuel cell.
- Achieved half-wave potential (*E*_{1/2}) of 0.83 V with atomically dispersed (AD) Fe-N-C in RDE testing, an increase of 0.02 V over the 2016 status.
- Improved PGM-free catalyst activity in an MEA: 16 mA/cm² at 0.90 V *V*_{*iR*-free} and 0.044 A/cm² at 0.87 V (H₂-O₂ fuel cell).

Characterization and Capability Development

- Determined >10× lower Fe dissolution rate with (AD) Fe-N-C than (CM+PANI)-Fe-C(Zn).
- Obtained direct evidence of a majority of Fe sites being atomically dispersed and on the (AD)Fe-N-C catalyst surface using STEM, a molecular probe and X-ray spectroscopies.
- Using STEM and nano-computed tomography, elucidated the source of performance limitations and identified pathways to improving (AD)Fe-N-C fuel cell performance.
- Synthesized 40 variations of (AD)Fe-N-C catalyst and characterized atomic structure using high-throughput X-ray diffraction and spectroscopy.

TABLE 1. Progress towards Meeting Technical Targets for PGM-free Electrocatalysts and MEAs for Transportation Applications

Characteristic	Units	DOE 2020 Electrocatalyst and MEA Targets	Current ElectroCat Status
H ₂ -air fuel cell performance	mA/cm ² @ 800 mV (measured)	300	100
PGM-free catalyst activity	mA/cm ² @ 900 mV <i>V</i> _{<i>iR</i>-free}	≥44	16

- Synthesized and characterized the composition of model thin-film FeN/C catalyst.
- Obtained 9 mV ORR half-wave potential agreement for Pt/C and <30 mV agreement for PGM-free catalyst between RDE and multi-channel flow double electrode measurements.
- Developed and utilized the capability to characterize by X-ray absorption fine structure (XAFS) the atomic structure of catalysts during heat treatment.
- Developed a PGM-free cathode performance model considering the effects of flooding, mass, and charge transfer and applied it to the (CM+PANI)-Fe-C cathode.

ORR Active-Site Activity and Durability Modeling

- Completed install, test, and linking of Vienna ab initio Simulation Package on dedicated computational cluster high-throughput software (Materials Simulation Toolkit and durability descriptor calculation automation [DDCA]) for structural relaxation calculation of ORR activity descriptor, and calculation of durability descriptor with output structure determined for input into ElectroCat data portal.
- Developed DDCA approach to determine the values of knock-on displacement threshold energy (KODTE), a proposed durability descriptor.
- Successfully completed initial set of library calculations for bulk-C, zig-zag edge-C, armchair edge-C structures (FeN₄, MnN₄, CoN₄, Fe₂N₅, MnCoN₅ with and without *OH ligand) including calculated ORR activities and KODTEs.
- Calculated NH and F ligand effects on OH binding energy, a proposed ORR activity descriptor.
- Generated additional Python scripts to aid in automation of computational cell set up (including addition of ligands to atoms in a given structure) and visualization (including 3D movies with tight integration between simulation output and 3D rendering software).



INTRODUCTION

The Energy Materials Network collates national laboratory capabilities into consortia accessible to industry and academia. The Electrocatalysis Consortium (ElectroCat) targets increasing U.S. competitiveness in manufacturing fuel cell electric vehicles and other fuel cell-based devices by addressing one of the greatest remaining challenges on the path to fuel cell electric vehicle commercialization: the high cost and limited availability of PGM catalysts for polymer

electrolyte fuel cells. In particular, the cost of noble metal catalysts restricts the ability to develop fuel cells that are cost-competitive with traditional hydrocarbon-based power sources. For that reason, electrocatalysts, especially for the cathode, represent the most pressing material barrier for fuel cell development and deployment. In response to the catalyst cost challenge, ElectroCat focuses on accelerating the deployment of PGM-free catalysts in fuel cells for fuel cell electric vehicles and other applications.

APPROACH

Developing effective PGM-free catalysts using cheaper, more abundant materials at an accelerated pace requires a systematic approach, by which potential catalysts are synthesized and analyzed rapidly and comprehensively using high-throughput, combinatorial methods that are in turn guided by computational studies and a fundamental knowledge of electrocatalysis. The effort is expected to benefit in a major way from the close collaboration of four national laboratories (ANL, LANL, National Renewable Energy Laboratory, and ORNL) with core competencies in PGM-free fuel cell catalyst development, including high-throughput synthesis and analysis. A consortium approach involving industry and university players provides rapid access to the unique capabilities housed at the national laboratories that make up ElectroCat, furthering meaningful progress towards the deployment of PGM-free catalysts, electrodes, and MEAs. Ultimately, the capabilities developed as part of ElectroCat could be applied to the broader advancement of electrocatalyst research, accelerating the discovery of interim solutions to the barriers posed by high PGM-content catalysts in other fields of use. As one of the first Energy Materials Network members, ElectroCat provides input on best practices and organizational support to the Energy Materials Network, thus facilitating the development of future consortia.

In addition to the development of PGM-free catalysts, ElectroCat focuses on creating the tools and catalyst information database critical to industrial deployment of PGM-free catalyst in fuel cells. ElectroCat national laboratory members use their combined expertise to refine and streamline the hardware and software tools necessary to model, analyze, and optimize PGM-free catalysts, electrode structures, and performance for a broad range of systems. These tools are expected to become enduring capabilities within the national laboratory system and to simultaneously grow the publicly-available data set as a resource. ElectroCat engages industry and university partners through funding opportunity announcements, providing an opportunity to further strengthen capabilities and advance innovative catalyst concepts. External partners also have the opportunity to approach the consortium and partner with laboratory experts through it by way of a CRADA.

RESULTS

Consortium Development

ElectroCat infrastructure support. LANL, with support from ANL, has been leading the coordination of TT/A for ElectroCat. The ElectroCat TT/A coordinator facilitates rapid and uniform contractual agreements between the laboratories themselves, as well as between the consortium and external users (e.g., agreements around intellectual property, indemnification, and/or payments to access laboratory resources). Current status of these agreements is:

- ElectroCat Industry Engagement Plan and Intellectual Property Management Plan.* ElectroCat Industry Engagement Plan, laying out guiding principles to be incorporated into a future Intellectual Property Management Plan, was sent to each of the ElectroCat member labs and has been finalized and agreed upon. We will begin circulating the Intellectual Property Management Plan for concurrence by each of the ElectroCat labs.
- Multi-Lab ElectroCat Non-Disclosure Agreement (NDA-17-0073).* The ElectroCat Multi-Lab NDA, modeled after the Fuel Cell Performance and Durability (FC-PAD) NDA, was sent to all of the ElectroCat member labs for execution of the multi-lab base NDA.
- ElectroCat CRADA Template.* A copy of the ElectroCat CRADA template was sent to each of the ElectroCat member labs for their review and concurrence. The template is based upon the LightMat Multi-Lab CRADA template, which all of the ElectroCat member labs have previously agreed upon. The template is available for use for any ElectroCat project award in which a CRADA may be necessary.
- Coordination Conference Call with TT/A Representatives.* A call with the TT/A representatives for each of the participating labs was held in March 2017 to ensure that all of the labs are aligned regarding the status of the various agreements and the consortia TT/A deliverables and timelines.

PGM-Free Catalyst Development

Catalysts with improved microporosity. Highly porous PGM-free catalysts, developed from a simple synthesis process using Zn salts (ZnCl_2) instead of Zn-metal organic frameworks, were further improved by removing spectator magnetic Fe species (magnetic purification). The combination of magnetic purification and removal of the hot-pressing step led to improved fuel cell performance in both kinetic and mass transport regions reaching a current density of 83 mA/cm^2 (120 mA/cm^2 at $0.80 \text{ V}_{\text{ir-free}}$). The kinetic region improvement is being attributed to an increased micropore

surface area, ca. $1,100 \text{ m}^2/\text{g}$, from Zn evaporation at an elevated heat-treatment temperature of $1,000^\circ\text{C}$ (Figure 1).

Catalysts with atomically dispersed transition-metal sites. Nitrogen-doped PGM-free catalysts containing atomically dispersed Fe, (AD)Fe-N-C, were successfully synthesized using a Zn-derived metal organic framework as the parent structure (Figure 2a). The synthesized (AD)Fe-N-C catalyst is composed of plate-shaped carbon structures, 30–50 nm in diameter and ca. 100–200 nm long. The carbon plates have a hierarchical micropore structure, critical for active site accessibility, formed from Zn evaporation during the high-temperature heat treatment. Characterization of (AD)Fe-N-C catalyst via high-angle annular dark-field STEM show well dispersed Fe atoms with minimal clustering. ORR activity measured in an electrochemical cell achieved a high half-wave potential ($E_{1/2}$) of 0.83 V vs. reference hydrogen electrode (RHE) (Figure 2b).

Direct detection of Fe sites. Nuclear resonance vibrational spectroscopy (NRVS) has been used to monitor structural perturbations of O_2 -accessible Fe sites via an O_2 -analogue gaseous probe molecule, nitric oxide (NO). This technique has provided new insight into the nature of Fe sites in PGM-free catalysts responsible for O_2 reduction. Isotope specificity of NRVS requires the use of ^{57}Fe to maximize signal intensity during data acquisition. ^{57}Fe -enriched (AD) ^{57}Fe -N-C catalyst was synthesized with atomically dispersed ^{57}Fe , with a minimal ^{57}Fe -clustering (Figure 3a). The (AD) ^{57}Fe -N-C was electrochemically reduced to change Fe^{3+} in the catalyst to Fe^{2+} for NO adsorption. The NRVS data of reduced and $\text{NO}_{(\text{g})}$ -treated (AD) ^{57}Fe -N-C catalyst are shown in Figure 3b. A new vibrational feature with

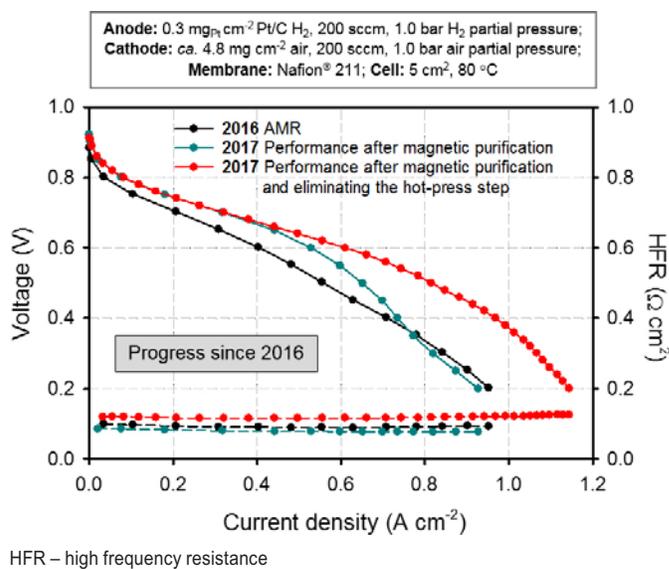


FIGURE 1. Improved H_2 -air fuel cell performance of Zn-derived (CM+PANI)-Fe-C(Zn) PGM-free catalyst (red curve) compared to 2016 performance reported at Annual Merit Review (AMR).

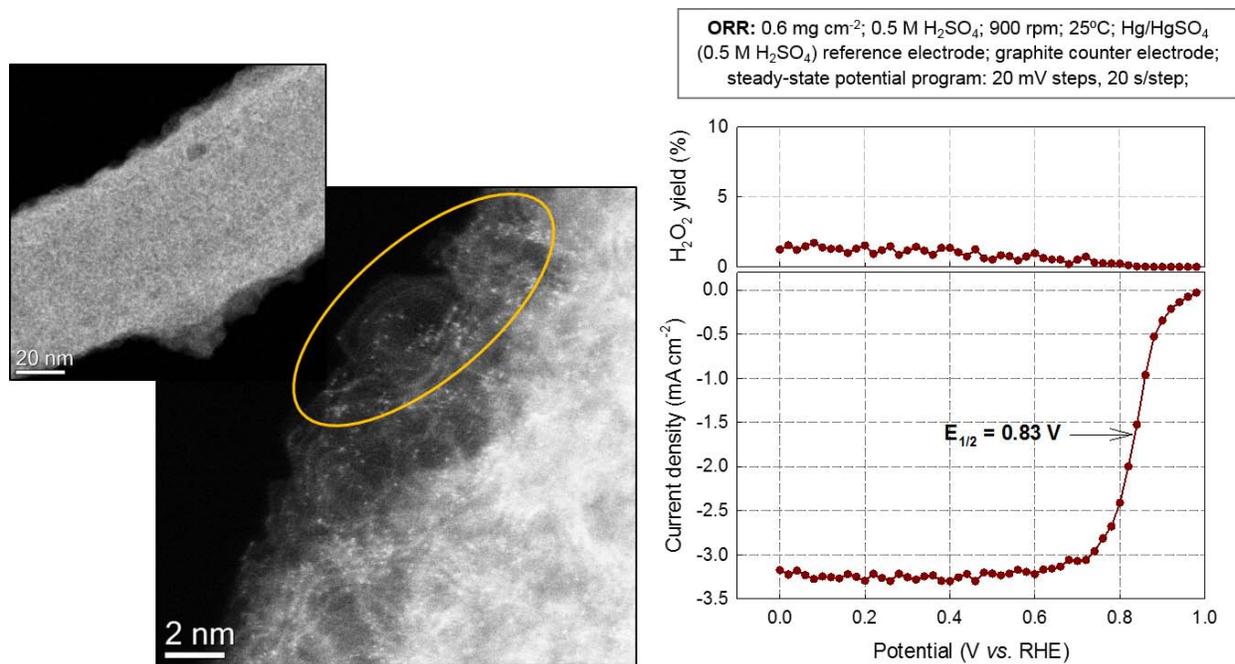
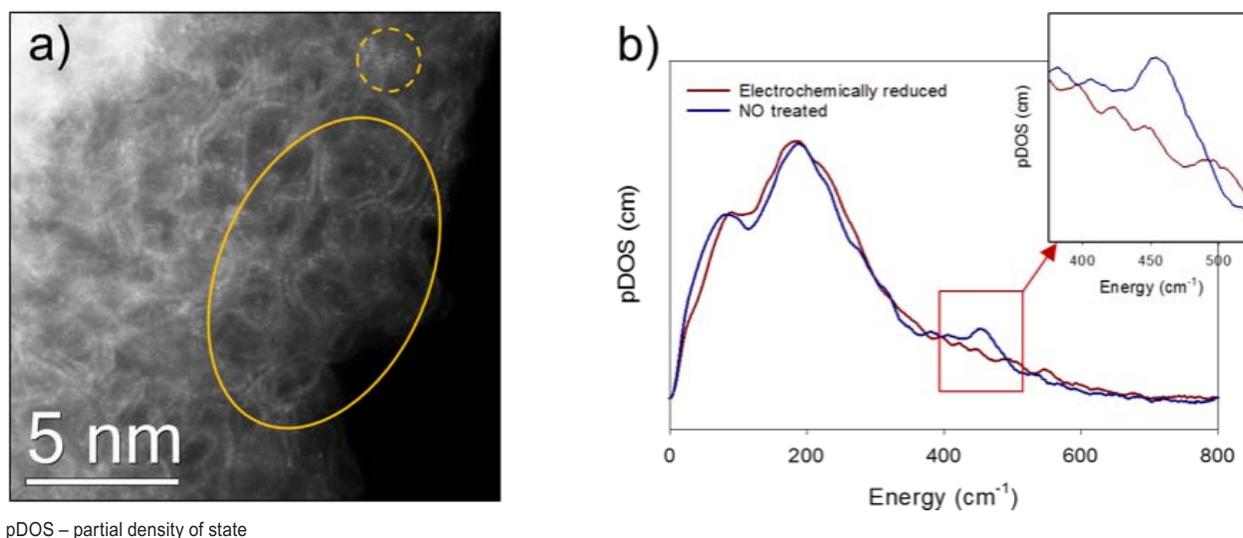


FIGURE 2. (a) High-angle annular dark-field STEM images of (AD)Fe-N-C catalyst showing a typical plate-shaped carbon structure (ca. 50 nm in diameter), as well as atomically dispersed iron over the carbon support with minimal Fe clustering (dark yellow); (b) ORR activity measured in an electrochemical cell demonstrating high ORR activity, $E_{1/2} = 0.83$ V vs. RHE.



pDOS – partial density of state

FIGURE 3. (a) High-angle annular dark-field STEM images of (AD)⁵⁷Fe-N-C catalyst showing atomically dispersed iron (solid yellow line), with some Fe-clustering (dashed yellow line); (b) NRVS data for reduced (AD)⁵⁷Fe-N-C (red) and NO_(g)-treated (AD)⁵⁷Fe-N-C (blue). Vibrational feature for NO-treated catalyst at a frequency of 450 cm⁻¹ likely corresponding to the Fe-NO bond stretch.

the NO_(g)-treated (AD)⁵⁷Fe-N-C catalyst is clearly seen at a frequency of 450 cm⁻¹. This vibrational feature is likely due to a Fe-NO bonding. This is a direct, surface-specific, evidence indicating that atomic Fe on the surface of the

catalyst can act as an adsorption site for O₂. Fe K-edge XAFS measurements before and during NO exposure also indicate that the majority of Fe in the catalyst is able to coordinate with NO.

ORR Active-Site Activity and Durability Modeling

Density functional theory relaxation calculations of all bulk-C, zig-zag edge-C, and armchair edge-C structures, as well as structures with ORR intermediates/adsorbates (OO, OOH, O, and OH) were completed using the Materials Simulation Toolkit. These calculations were then used for the determination of the thermodynamic limiting potential, U_p , which serves as the ORR activity descriptor for a specific atomic-scale structure. DDCA scripts were created enabling high-throughput calculation of KODTE for arbitrary input atoms over a relevant range of energies. These scripts were integrated with the Atomic Simulation Environment and Python Materials Genomics (pymatgen) codes. KODTEs, the proposed durability descriptors that incorporate kinetics of bond breaking and atomic detachment, were calculated for all structures using the developed software. These calculations confirmed that the DDCA-based descriptor methodology fits well with the high-throughput high pressure cell paradigm and, that this descriptor is able to distinguish changes in durability descriptor with changes in atomic scale structure. Particularly, multi-metal atom structures ($M_1M_2N_5$) were found to be less durable than their single-metal atom (MN_4) counterparts. Additionally, it was determined that N atoms, particularly those at edges, defined the lowest KODTE for all explored structures, independent of metal speciation and structure.

High-Throughput Techniques for Synthesis and Characterization of PGM-Free Catalysts

A high-throughput and, where possible, combinatorial approach to synthesis, characterization, ORR-activity measurement, electrode fabrication, and fuel cell performance testing is being utilized to expedite progress toward achieving the ElectroCat goals (Figure 4). The previously mentioned LANL (AD)Fe-N-C catalyst was chosen as the first catalyst system for this approach. This system was selected due to the observed high ORR activity in RDE testing ($E_{1/2} = 0.83$ V vs. RHE) and because only a small fraction of the possible composition and synthesis parameters have been explored using batch synthesis methods. The parameters varied in the high-throughput synthesis were the Fe-to-Zn ratio in the precursors, the identity of the Fe salt, and the heat-treatment temperature. The robotic system at ANL was utilized to rapidly synthesize forty precursors in which these three parameters were varied. After combinatorial heat treatment, the structural properties of the forty powders were determined using X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS). For a subset of these precursors, a capability was developed and utilized to determine the atomic structure of six samples simultaneously during heat treatment using Fe K-edge XAS. These experiments showed that the predominant Fe species

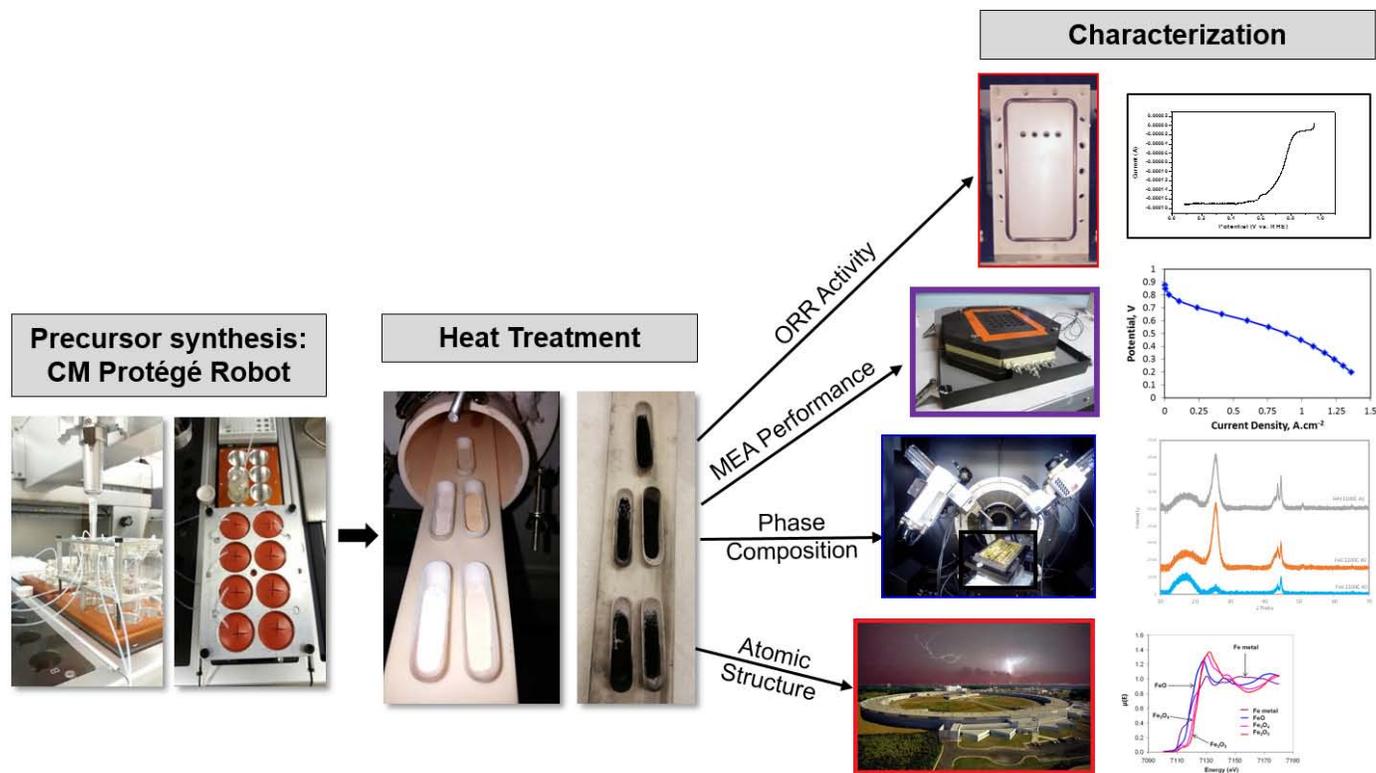


FIGURE 4. ANL high-throughput synthesis and characterization system: robotic system, simultaneous heat treatment, high-throughput structural characterization using X-ray diffraction and XAFS, and multi-channel flow double electrode cell for ORR activity characterization.

present in the active catalyst is formed in the 620–700°C temperature range during the increasing temperature heat-treatment step (Figure 5). Trends in the phase composition and atomic structure were discerned as a function of Fe precursor, Fe content, and heat treatment temperature. Examples of these trends were that the Fe nitrate precursor resulted in Fe species with a lower oxidation state than those derived from Fe sulfate and Fe acetate precursors and that higher heat-treatment temperature and iron content result in larger amounts of crystalline iron carbide. The ORR activity is currently being characterized using a multi-channel flow double electrode cell, which allows the aqueous hydrodynamic measurement of ORR activity of four samples simultaneously. The goal is to correlate ORR activity and structural composition of the catalysts.

Capability Development

ElectroCat is developing several capabilities that show potential to impact PGM-free electrocatalyst development. One such capability is the fabrication and characterization of model systems, such as thin films deposited on planar substrates. The purpose of this activity is to elucidate the nature of the active site and to potentially discover material compositions with enhanced ORR activity. National Renewable Energy Laboratory has developed the capability to deposit films of uniform or gradient composition or thickness (5–100 nm) of Fe and N on a planar substrate using physical vapor deposition (Figure 6). Characterization of these films shows that Fe-N bonds are formed in the film and C-N bonds are formed at the interface with the glassy carbon substrate, with the likely formation of the proposed active moiety, FeN_4 , in the carbon matrix. Further spectroscopic and electrochemical characterization are underway.

Another capability being developed and demonstrated in ElectroCat is combinatorial fuel cell performance testing. The purpose of this activity is to accelerate the optimization of the electrode composition and structure for PGM-free catalysts by developing methods for the high-throughput synthesis and deposition of catalyst-ionomer-solvent inks, and measuring ORR activity and fuel cell performance. Two test fixtures are being evaluated for this purpose: a combinatorial 25-electrode setup with segmented flow field, gas diffusion layer, and electrode (NuVant) and a segmented current collector/flow field, with 121 individually-addressable segments, with a common/continuous gas diffusion layer and electrode. The 25-electrode setup shows identical iR -corrected hydrogen-air polarization curves for the 25 electrodes and measures are underway to improve the electrode-to-electrode resistance uniformity. The latter set-up showed significant cross-talk between the 121 segments and cell redesign is underway to address the cross-talk issue.

CONCLUSIONS AND UPCOMING ACTIVITIES

The following are highlighted conclusions from the ElectroCat activities thus far:

- An Fe-N-C catalyst, (AD)Fe-N-C, has been developed in which the majority of Fe sites are atomically-dispersed and on the catalyst surface, as determined by low-voltage, atomic-scale STEM imaging, and X-ray absorption and vibrational spectroscopies with probe molecules.
- The Fe sites within the atomically dispersed catalyst are more stable against dissolution than catalysts made via

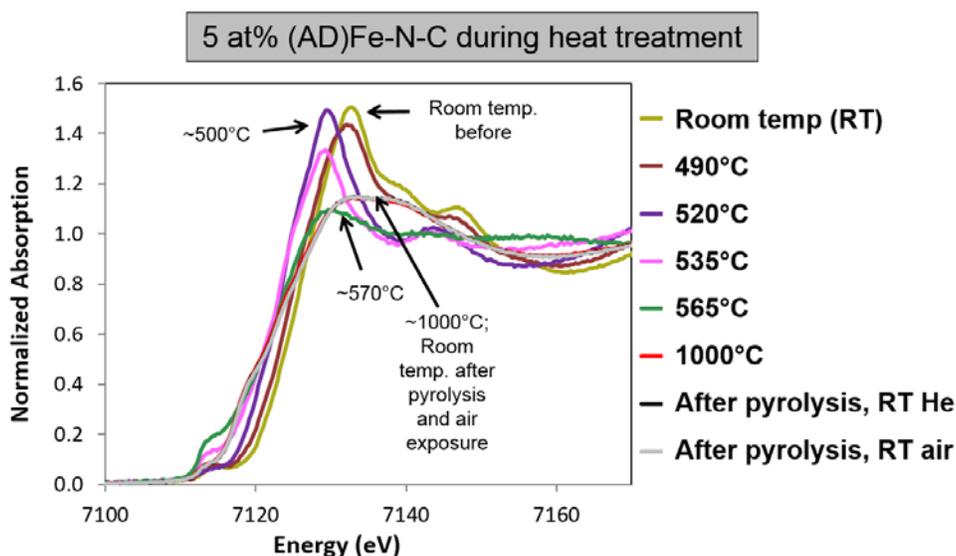
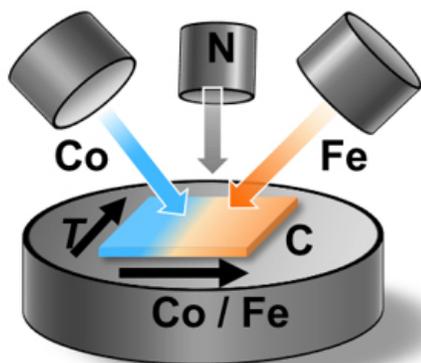


FIGURE 5. In situ XAFS during heat treatment showing Fe species found in ORR active catalysts forming at ~620–700°C.

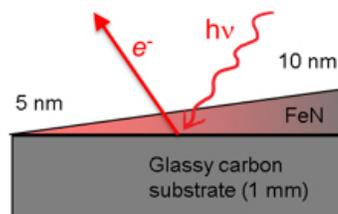
PVD Synthesis



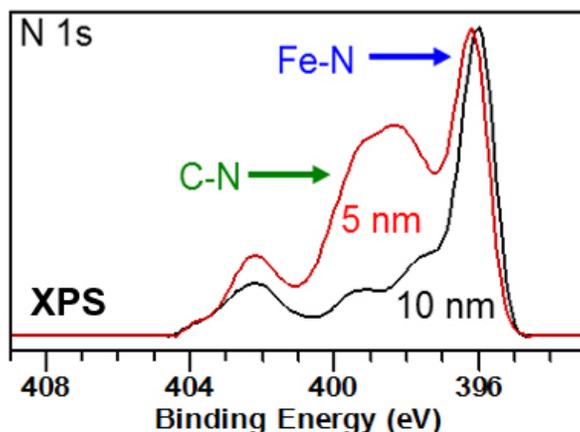
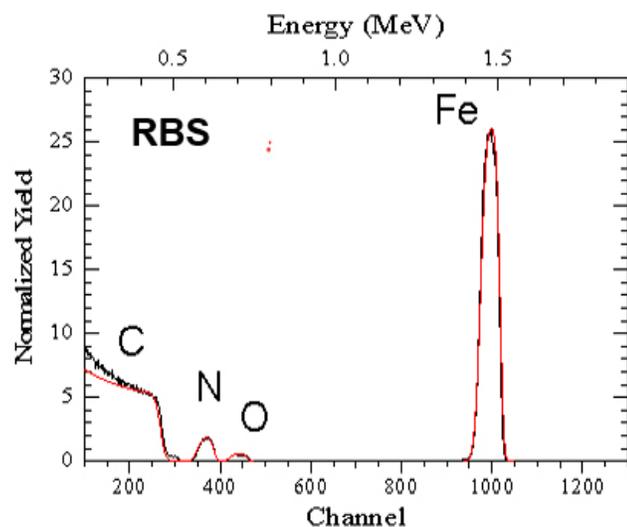
Thick film to determine deposition conditions

FeN	100 nm
Glassy carbon	1 mm

FeN/C interface by thin film deposition



Fe-N composition controlled by Fe, N, T



PVD – physical vapor deposition; RBS – Rutherford back scattering

FIGURE 6. Synthesis of model systems via physical vapor deposition on a glassy carbon substrate. XPS characterization of these films (bottom right) show presence of Fe-N and C-N bonds.

heat treatment of Fe-polyaniline-cyanamide, with over an order of magnitude lower Fe dissolution rates.

- A computation durability descriptor was identified and applied to various proposed active site configurations, showing that edge atoms in an “armchair” configuration are the least stable and that the nitrogen in the structures is the most susceptible to damage.
- An H₂-air fuel cell performance with a PGM-free cathode, 83 mA/cm² at 0.80 V (120 mA/cm² at 0.8 V_{iR-free}), was obtained by increasing the micropore surface area, removing spectator magnetic Fe species, and eliminating the hot-pressing step in cell fabrication.

The following are the remaining challenges and barriers in developing and implementing PGM-free ORR catalysts:

- Need for improvement in ORR activity to reduce cathode thickness and lower cost of other stack components.
- Insufficient long-term stability and performance durability under steady-state and load-cycling conditions.
- Limited understanding of the ORR mechanism, nature of the ORR active site and mechanism of catalyst degradation preventing rational design of next-generation PGM-free catalysts.
- Low volumetric density of active sites.

- Electrode design and component integration to provide adequate ionic, electronic, and mass transport to and from active sites.
- Replacement of Fe in catalyst with another PGM-free transition metal not catalyzing hydroperoxyl radical formation and ionomer degradation.
- Integration with existing automotive fuel cell stack and system technology.

The focus of future work to address these challenges includes the following.

Consortium Development

- Incorporate collaborators from DE-FOA-0001647 into ElectroCat and coordinate activities of all ElectroCat partners.
- Update ElectroCat website with information from funding opportunity announcement projects, status of capabilities, publications.
- Implement capabilities to mint digital object identifiers and other identifiers with persistent landing pages for datasets and to support automated data capture and publication.
- Document ElectroCat data sources: (i) formats, (ii) associated metadata, (iii) sharing needs, and (iv) dataset comparison or integration needs.
- Execute intellectual property management plan and material transfer agreements.

Performance and Durability Improvement

- Advance activity of atomically dispersed catalysts by maximizing concentration and accessibility of active centers through (i) the development of novel synthesis approaches, (ii) optimization of hierarchical pore-size and ionomer distribution, and (iii) decreasing electrode tortuosity.
- Explore (AD)Fe-N-C parameter space for improved performance and durability using high-throughput activity, durability, and performance testing of 40 materials synthesized to date.
- Determine primary factors governing the durability of PGM-free catalysts, concentrating predominantly on homogenous and thus easier to study materials.
- Further develop surface-specific methods for the ORR active-site determination.

Characterization and Capability Development

- Active-site identification, influence of Fe-to-N-to-C ratio on ORR activity, and influence of synthesis parameters on active-site formation: (i) thin-film model systems; (ii) ex situ, in situ, and operando X-ray spectroscopies

and electron microscopy; (iii) high-throughput catalyst synthesis, characterization, and activity testing.

- ORR kinetics, mechanisms, and reactant/product transport: (i) in-cell polarization and impedance measurements as a function of oxygen partial pressure, temperature, cell voltage, etc., with systematic extraction of ORR kinetic and transport parameters, including oxygen/water transport in gas channel, diffusion media and electrodes; (ii) electrochemical techniques in aqueous electrolytes.
- Degradation mechanisms/durability: (i) online ICP-MS-RDE to correlate activity with catalyst component loss; (ii) ex situ and in situ tomography, spectroscopy, and microscopy; (iii) voltage-loss analysis using polarization curves and impedance spectroscopy.
- Electrode optimization: (i) segmented cell combinatorial studies of electrode performance coupled with high-throughput catalyst-ink synthesis and deposition; (ii) tomography and electron microscopy/energy dispersive X-ray visualization of solid, pore, and ionomer distribution coupled with electrode transport modeling.

ORR Active-Site Activity and Durability Modeling, Including High-Throughput

- Further analysis of ligand modification effects.
- Improved, automated analysis and structure generation scripts to determine limiting potential and allow for initial rotation of ligand via input Euler angles.
- Application to other proposed structures and ligands, particularly those from industry, national labs, and academia, including non-covalently bonded edge Fe structure and NO and CO ligands.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Argonne Director's Award, Theodore Krause, Sheldon Lee, and Deborah Myers, Argonne National Laboratory, June 2017.
2. "ORNL Mentor of Early Career Researcher Award," Karren More, November 2016.

FY 2017 PUBLICATIONS/PRESENTATIONS

Publications

1. "Resolving Electrode Morphology's Impact on Platinum Group Metal Free Cathode Performance using Nano-CT of 3D Hierarchical Pore and Ionomer Distributions;" S. Komini Babu, H.T. Chung, P. Zelenay, S. Litster, *ACS Appl. Mater. Interfaces*, 8 (48), 32764–32777, 2016.

2. “Direct Simulations of Coupled Transport and Reaction on Nano-Scale X-Ray Computed Tomography Images of Platinum Group Metal-Free Catalyst Cathodes;” S. Ogawa, S. Komini Babu, H.T. Chung, P. Zelenay, and S. Litster, *ECS Trans*, 75 (14), 139–146, 2016.
3. “Linking Structure to Function: The Search for Active Sites in Non-Platinum Group Metal Oxygen Reduction Reaction Catalysts;” E.F. Holby and P. Zelenay, *Nano Energy*, 29, 54–64 (2016).
4. “Heat-Treated Non-Precious Metal Catalysts for Oxygen Reduction;” H. Chung, G. Wu, D. Higgins, P. Zamani, Z. Chen, and P. Zelenay, in *Electrochemistry of N4 Macrocyclic Metal Complexes*, Volume 1: Energy, J. H. Zagal and F. Bedioui (eds.), pp. 41–68, Springer, 2016.
5. “Non-Precious Metal Fuel Cell Cathodes: Catalyst Development and Electrode Structure Design;” P. Zelenay, H. Chung, U. Martinez, E. Holby, X. Yin, G. Purdy, L. Ling, J. Ziegelbauer, M. Odgaard, J.H. Brewster, D. Schlueter, S. Litster, S.K. Babu, M. Neidig, J. Kehl, J. Kneebone, Z. Chen, P. Zamani, X. Fu, J.-Y. Choi, K.L. More, and D. Cullen; US Department of Energy, Hydrogen and Fuel Cells Program; 2016 Annual Progress Report; https://www.hydrogen.energy.gov/pdfs/progress16/v_a_1_zelenay_2016.pdf

Patent Applications

1. H.T. Chung, L. Lin, and P. Zelenay; “Zinc-derived Microporous Structure in Non-Precious Catalysts for Polymer Electrolyte Fuel Cell Cathodes;” filed November 14, 2016.
2. G. Wu and P. Zelenay; “Non-precious Fuel Cell Catalysts Comprising Polyaniline” (divisional of U.S. Application No. 13/267,579); filed October 17, 2016.

Presentations

1. Department of Chemical and Biomolecular Engineering, University of Tennessee, Knoxville, Tennessee, March 27, 2017. Title: “Platinum Group Metal-free Electrocatalysts for Oxygen Reduction in Fuel Cells;” P. Zelenay (*invited lecture*).
2. Technische Universität Darmstadt, Graduate School of Energy Science and Engineering, Darmstadt, Germany, February 7, 2017. Title: “PGM-free Electrocatalysis Research at Los Alamos;” P. Zelenay (*invited lecture*).
3. 7th International Conference on Fundamentals and Development of Fuel Cells (FDFC 2017), Stuttgart, Germany, January 31–February 2, 2017. Title: “Oxygen Reduction on PGM-free Electrocatalysts;” P. Zelenay*, H.T. Chung, U. Martinez, L. Lin, X. Yin, G.M. Purdy, and E. F. Holby (*invited lecture*).
4. Beijing Forum 2016 on Electrochemical Frontier, Wuhan, China, December 6–8, 2016. Title: “Recent Progress in ORR Electrocatalysis on Me-N-C Catalysts;” U. Martinez, J. Dumont, L. Lin, X. Yin, G.M. Purdy, E.F. Holby, H.T. Chung, and P. Zelenay* (*invited lecture*).
5. School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan, China, December 6, 2016. Title: “Oxygen Reduction Reaction at Platinum Group Metal-free Fuel Cell Electrocatalysts;” P. Zelenay (*invited lecture*).

6. DGIST Global Innovation Festival (DGIF), Daegu, South Korea, December 1–2, 2016. Title: “Fuel Cell Electrocatalysis: Accomplishments and Challenges;” P. Zelenay (*invited lecture*).
7. Department of Energy Systems Engineering, Daegu Gyeongbuk Institute of Science Technology (DGIST), Daegu, South Korea, November 30, 2016. Title: “A Few Highlights from PGM-free ORR Catalysis Research at Los Alamos National Laboratory;” P. Zelenay (*invited lecture*).
8. Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Gothenburg, Sweden, November 24, 2016. Title: “Platinum Group Metal-free ORR Catalysts for Fuel Cells Applications;” P. Zelenay (*invited lecture*).
9. DOE Energy Efficiency and Renewable Energy Office, Fuel Cell Technologies Office, November 8, 2016. Title: “FCO Lab Consortia Overview: ElectroCat and HyMARC;” D. Myers, M. Allendorf, and P. Zelenay, (*invited webinar*). http://energy.gov/sites/prod/files/2016/11/f34/cto_webinarslides_electrocat_hymarc_consortia_overview_110816.pdf
10. Fuel Choices Summit, Tel Aviv, Israel, November 2–3, 2016. Title: “Panel 2: A Global Fuel Cell Technology Roadmap;” P. Zelenay, D. Stelten, L. Elbaz (S. Satyapal – moderator), (*invited webinar*).
11. Fuel Cells Workshop, Bar-Ilan University, Ramat Gan, Israel, November 1, 2016. Title: “PGM-free ORR Catalysts for Fuel Cell Applications;” P. Zelenay* (*invited lecture*).
12. Pacific Rim Meeting on Electrochemical and Solid-State Science (PRiME), Honolulu, Hawaii, October 2–7, 2016. Title: “Graphene Oxide-Based Non Precious Metal Catalysts for Oxygen Reduction Reaction with Improved Selectivity and Performance;” J.H. Dumont*, U. Martinez, G.M. Purdy, A. M. Dattelbaum, P. Zelenay, P. Atanassov, A. Mohite, and G. Gupta.
13. Pacific Rim Meeting on Electrochemical and Solid-State Science (PRiME), Honolulu, Hawaii, October 2–7, 2016. Title: “Binary Fe-Free Transition Metal Catalysts for the Oxygen Reduction Reaction;” U. Martinez*, E.F. Holby, J.H. Dumont, and P. Zelenay.
14. Pacific Rim Meeting on Electrochemical and Solid-State Science (PRiME), Honolulu, Hawaii, October 2–7, 2016. Title: “Zinc-Derived Microporous Structure in Non-Precious Metal Catalysts for Polymer Electrolyte Fuel Cell Cathodes;” L. Lin*, H.T. Chung, X. Yin, U. Martinez, and P. Zelenay.
15. Pacific Rim Meeting on Electrochemical and Solid-State Science (PRiME), Honolulu, Hawaii, October 2–7, 2016. Title: “High-Temperature Synthesized PGM-Free Oxygen Reduction Reaction Catalyst;” H.T. Chung*, D.A. Cullen, B. Sneed, L. Lin, X. Yin, U. Martinez, G.M. Purdy, K.L. More, and P. Zelenay.
16. Pacific Rim Meeting on Electrochemical and Solid-State Science (PRiME), Honolulu, Hawaii, October 2–7, 2016. Title: “Resolving Active Sites and Porosity in PGM-Free Catalysts by Electron Microscopy;” D.A. Cullen*, B. Sneed, K.L. More, J.H. Brewster, M. Odgaard, H.T. Chung, and P. Zelenay.
17. Pacific Rim Meeting on Electrochemical and Solid-State Science (PRiME), Honolulu, Hawaii, October 2–7, 2016. Title: “Modeling PGM-Free Active Site Structures: Activity and Durability;” E.F. Holby*, U. Martinez, H.T. Chung, and P. Zelenay.

- 18.** Pacific Rim Meeting on Electrochemical and Solid-State Science (PRiME), Honolulu, Hawaii, October 2–7, 2016. Title: “Magnetic Purification of PGM-Free Catalysts;” X. Yin*, U. Martinez, H.T. Chung, L. Lin, and P. Zelenay (poster presentation).
- 19.** Pacific Rim Meeting on Electrochemical and Solid-State Science (PRiME), Honolulu, Hawaii, October 2–7, 2016. Title: “Imaging Fuel Cell Components: From Flow Field Channels to Catalyst Layers;” D. Spornjak, R. L. Borup, D. S. Hussey, P. Zelenay, and R. Mukundan (*invited lecture*).
- 20.** Pacific Rim Meeting on Electrochemical and Solid-State Science (PRiME), Honolulu, Hawaii, October 2–7, 2016. Title: “Direct Simulations of Coupled Transport and Reaction on Nano-Scale X-Ray Computed Tomography Images of Platinum Group Metal-Free Catalyst Cathodes;” S. Ogawa*, S. Komini Babu, H.T. Chung, P. Zelenay, and S. Litster.
- 21.** Workshop on Material Challenges for Fuel Cell & Hydrogen Technologies, Grenoble, France, September 19–21, 2016. Title: “PGM-free ORR Catalysts: State of the Art and Recent Progress;” P. Zelenay*, H.T. Chung, U. Martinez, L. Lin, Xi Yin, G. M. Purdy, and E.F. Holby (*invited plenary lecture*).
- 22.** 67th Annual Meeting of the International Society of Electrochemistry, The Hague, Netherlands, August 21–26, 2016. Title: “Recent Progress in the Development of Non-Precious Metal ORR Catalysts for Fuel Cells;” P. Zelenay*, H.T. Chung, U. Martinez, L. Lin, X. Yin, G.M. Purdy, and E.F. Holby (*invited lecture*).
- 23.** ElectroCat Workshop, Argonne National Laboratory, Lemont, Illinois, July 26, 2017, Title: “Overview of high-throughput techniques as applied to fuel cell catalysts and electrodes”, D. Myers.
- 24.** ElectroCat Workshop, Argonne National Laboratory, Lemont, Illinois, July 26, 2017, Title: “Summary of ElectroCat experimental capabilities”, P. Zelenay, D. Myers, K. More, and H. Dinh.
- 25.** ElectroCat Workshop, Argonne National Laboratory, Lemont, Illinois, July 26, 2016, Title: “DFT modeling of PGM-free catalyst activity and durability”, E.F. Holby.
- 26.** ElectroCat Workshop, Argonne National Laboratory, Lemont, Illinois, July 26, 2016, Title: “Electrode microstructure and transport modeling”, F. Cetinbas.
- 27.** ElectroCat Workshop, Argonne National Laboratory, Lemont, Illinois, July 26, 2016, Title: “Data management and technology transfer/agreement approaches”, I. Foster and L. Barber.
- 28.** ElectroCat Workshop, Argonne National Laboratory, Lemont, Illinois, July 26, 2016. Title: “State of the art of PGM-free catalyst activity and durability;” P. Zelenay.
- 29.** U.S. Department of Energy, Energy Efficiency and Renewable Energy, Fuel Cell Technologies Program, 2016 Merit Review and Peer Evaluation Meeting, Washington, D.C., June 6–10, 2016. Title: “Non-Precious Metal Fuel Cell Cathodes: Catalyst Development and Electrode Structure Design;” P. Zelenay (*DOE invited lecture*). https://www.hydrogen.energy.gov/pdfs/review16/fc107_zelenay_2016_o.pdf

REFERENCES

- 1.** “Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan,” updated May 2017, <https://energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>.